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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> ATTRITION RESISTANT THIN FILM CATALYST AND METHOD OF PREPARATION  <b>(57) Abstract</b>  A thin film of catalyst is applied to a substrate by use of a coating composition that includes a film-forming polymer to reduce cracking of the coating during the coating process, resulting in an attrition resistant thin film product. Polyvinyl pyrrolidone and hydropropyl methylcellulose are used as film forming polymers in the examples.		

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**ATTRITION RESISTANT THIN FILM  
CATALYST AND METHOD OF PREPARATION**

This invention was made with United States Government support under  
5 the ATP award number 70NANB5H1141 awarded by the National Institute of  
Standards and Technology, U.S. Department of Commerce.

**Background of the Invention**

The present invention relates to solid catalysts and to a method for  
10 preparation thereof. Specifically, the invention relates to a method of producing  
catalysts or catalyst precursors comprising a substrate which is usually  
catalytically inactive, and a thin film of catalyst or catalyst precursor.

The use of solid catalyst comprised of small particles containing  
catalytically active materials on the surface thereof are desirable for a wide variety  
15 of chemical reactions. As one example, it would often be desirable in certain  
catalyzed chemical reactions which are historically catalyzed by liquid catalyst to  
replace the liquid catalysts with solid catalyst to simplify the process, and to  
reduce environmental concerns associated with such liquid catalyst. As one  
example, the production of highly branched hydrocarbons such as  
20 trimethylpentane for use as gasoline blending components for octane enhancement  
traditionally involves alkylation using conventional strong liquid phase catalysts  
such as hydrofluoric or sulfuric acid. The use of these liquid acid catalysts creates  
certain environmental concerns. With hydrofluoric acid, the concern is the  
possibility of the release of toxic vapors. With sulfuric acid, there is no acute  
25 toxic release problem, but there is the need to truck away and treat the waste acid  
which involves thermal decomposition and preparation of fresh acid. The  
transportation of the waste and fresh acid is closely regulated to prevent spills.

In view of the potential problems with the liquid acid catalysts such as  
used for alkylation, it is desirable to use less hazardous and toxic and more  
30 environmentally acceptable catalysts. Specifically, it is desirable to use solid  
catalysts rather than liquid catalysts. However, the use of solid catalysts at least

for certain reactions such as alkylation has not been very successful. The main problem is the very short catalyst life which is sometimes measured in terms of hours, or possibly a few days.

One type of catalyst which holds promise for such reactions comprises a catalytically inert core which is covered with a shell comprised of, or containing, the catalytically active material. Such thin film or shell catalysts are not in themselves novel and have been disclosed in patents such as U.S. Pat. Nos. 4,394,251; 4,793,980; 4,427,577; 4,677,089; 4,378,308; 5,082,814; 5,200,382 and European Patent Application No. 323,735. These supported catalysts of the prior art are characterized by a number of factors which influence their usefulness. One is the penetration of the catalytic coating into the core when a porous core material such as alpha-alumina is used. It is well known to those skilled in the art that porous supports can be impregnated with a solution containing a catalyst precursor which fills the pores within the oxide support. This method is often referred to as the dry impregnation method or the incipient wetness method. Impregnation using slurries containing colloidal particles, *i.e.*, a sol, using this prior art technique shows that there is substantial penetration of the sol into the substrate. This, as well as the coating techniques themselves, result to varying degrees in a non-uniform coating thickness. In addition, prior art preparation methods result in a range of pore diameters and in films of various thicknesses. The pore diameters within the film and the film thicknesses strongly influence the rate of diffusion of the reactants to the active sites in the pores and of the reaction products out of the film. As the core diameters decrease and as the film thicknesses increase, the diffusion of reactants and products will lead to deleterious reaction products which foul the catalyst surface. This concept of catalyst deactivation has been recognized in the published literature. A high flux of reactants and products is necessary to obtain a high number of molecules reacted per unit of time for each active catalyst site and, more importantly, to suppress undesired reaction products which foul the surface. This is partially due to the long residence time within the intricate network of pores resulting in unwanted side reactions in conventional catalyst or in thin film catalysts of

uncontrolled film thickness. Although it has been known that it would be desirable to concentrate the catalyst sites in a thin layer on the surface of a core particle, the techniques for forming such a uniform layer have not been satisfactory. Therefore, we have sought a method of catalyst preparation where it  
5 would be possible to prepare thin films, or thin shells, of controllable thickness comprising catalysts or catalytic supports on a wide variety of substrates.

In accordance with an aspect of the present invention, there is provided a process for providing a catalyst or catalyst precursor on a substrate or support in the form of a thin film, wherein the catalyst or precursor is coated onto the  
10 substrate by use of a coating composition comprising at least one of a catalyst support (with or without a catalyst or catalyst precursor), unsupported catalyst precursor or unsupported catalyst (hereinafter sometimes referred to individually and collectively as a "catalyst element") in the form of particles dispersed in water and/or a polar non-aqueous solvent, preferably water, and at least one film forming  
15 polymer dissolved and/or dispersed in the water and/or polar non-aqueous solvent, wherein when the catalyst element is an unsupported catalyst the unsupported catalyst is other than a metal sol.

Applicant has found that the addition of a film forming polymer to the coating composition provides an improved coating of catalyst element on the  
20 substrate or support; in particular, cracking or spalling of the coating is reduced or eliminated. Thus, there is an improved adherence of the coating to the support or substrate leading to an overall robust composition which is highly attrition resistant, and which is useful in such systems as liquid fluidized bed, slurry system, or a gas phase fluidized bed system.

25 The coating composition for producing a thin film or shell of catalyst element on a substrate or support (preferably a particulate substrate or support), as hereinabove indicated, includes a film forming polymer. As representative examples of monomers which may be employed to produce film forming polymers (either a homopolymer or a copolymer formed from two or more  
30 monomers) there may be mentioned: vinyl pyrrolidone, acrylic acid; methacrylic acid; hydrophilic esters of acrylic and methacrylic acid, such as esters of

polyglycols, glycerol or sugars; alkylene oxide; maleic acid; styrenesulfonic acid; acrylamide and N-substituted acrylamide; vinyl alcohol; or methylvinylether. They can also be based on water-soluble polysaccharides, such as dextrans, dextrane sulfate, hydroxypropyl methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, chondroitin sulphate or hyaluronic acid, etc. Dispersible polymers include butyl rubber and carboxylated butyl rubber, polystyrene and polystyrene with divinylbenzene cross-linking agents and these polymers with ethylvinylacetate incorporated to enhance water dispersability. Also, polybutylrubber resin, and styrene butadiene resins, polyphenylsulfide resins, and polyacrylonitrile resins. Other dispersible resins include polymethacrylate resins, etc.

The polymer(s) is dissolved and/or dispersed in the liquid portion of the coating composition and, therefore, the polymer is one which is soluble or dispersible in such liquid under the coating conditions. The polymer is also preferably capable of forming a web or complex of filaments in the coating of catalyst element on the substrate.

The polymer is added to the composition in an amount effective to prevent cracking, or spalling, of the coating on the substrate during the drying step in the coating process, or cracking, or spalling during subsequent drying or heat treatment steps to convert the film to a functional catalyst. These steps can include such treatment steps as treatment in flowing air or inert gases, such as helium or nitrogen, treatment in air diluted with an inert gas with/without steam present, treatment in a reducing gas such as hydrogen, carbon monoxide, or hydrocarbon containing gases. The polymer is generally present in the composition in an amount of from 0.01% to 20% and preferably 0.2 to 5 percent by weight. The film forming polymer is used in an amount such that the film forming polymer is incorporated or intermixed in the layer(s) of catalyst element on the support.

The invention involves an improvement in solid catalysts and particularly to the method for forming such catalysts. More specifically, the catalyst comprises a substrate, which is usually catalytically inert (the catalyst substrate is generally an inorganic material), on which is deposited and bonded a thin shell or



film of the catalyst element. The catalyst element is also generically inorganic. However, carbon-based supports can also be used, such as, carbon blacks, graphite, carbon molecular sieves, and inorganic carbides, such as SiC, Si<sub>3</sub>N<sub>4</sub>, iron carbides, tungsten carbides, etc. In a preferred embodiment, the thin shell is formed by a deposition process which uses a fluidized bed coating technique which involves repeatedly applying and drying small quantities of a coating composition comprising an aqueous slurry containing the catalyst element, wherein the slurry is in the form of an aqueous colloidal dispersion, or sol, or where the slurry contains very fine, non-colloidal particles preferably mixed with colloidal particles wherein a film forming polymer is dissolved and/or dispersed in the water. Incremental layers of one or more catalysts mixed throughout the thin film, or formed as separate layers of different catalysts within the film are deposited and dried to form the final thin shell which has a highly uniform thickness which is usually less than 250 microns, and more preferably less than 100 microns. The catalyst material can be a part of the shell forming material, or can be added to the formed shell, or can be formed by subsequent reaction with the formed shell. The catalyst particles formed by the present invention may be used for a wide variety of chemical reactions including the alkylation reactions previously discussed.

## **Brief Description of the Drawings**

Figure 1 is a graphical representation of the effect of using the film forming polymer, polyvinyl pyrrolidone (PVP) for dip coating;

Figures 2 and 3 are graphical representations of the effect of using PVP for coating under shear conditions; and

Figure 4 is a graphical representation of the effect of using OPADRY, (Colorcon Inc.) containing hydroxypropyl methyl cellulose for coating under high shear conditions.

## **Description of the Preferred Embodiments**

The substrate onto which the thin film of catalyst element is coated is preferably a catalytically inactive material, with a thin shell formed on the

substrate being comprised of the catalyst element. The substrate is preferably in particulate form and usually comprises alpha alumina particles but may be formed from particles or microspheres of transitional alumina, silica, zeolites, zirconia, titania, clay minerals, silicon carbide or their mixtures. The substrate may also be  
5 formed from non-porous materials such as hollow spheres of inorganic materials, such as silica or alumina, metal, clay minerals, silicon carbide, silicon nitride, or carbon-based materials such as graphite. In the context of the present invention, catalytically inert means inert with respect to the particular reaction in which the catalyst is being used even though the substrate may have catalytic activity with  
10 respect to some other reaction. Although the substrate is preferably a particle, the present invention is not limited to a substrate in the form of a particle.

The invention involves a procedure for forming the thin shell or film of catalyst element on a substrate and the catalyst element which is formed by the use of that technique produces a shell of and controllable thickness over the  
15 substrate.

In a particularly preferred embodiment, the catalyst element is coated on the support or substrate by either a rotating disk coater or by a fluidized bed coating technique which has been used in other technologies, particularly in the pharmaceutical industry for forming coatings of drugs onto benign sugar core  
20 materials which act as seeds for the drug coating. The general principle of the fluidized bed coating process employed in the present invention is that the particles to be coated are suspended in an air stream designed to fluidize the particles and carry them through an atomized spray of the coating material. In the preferred arrangement, there is a cyclic flow of the particles past a nozzle  
25 arrangement such that only a very thin, partial coating is produced on each pass of the particles through the atomized spray in the coating zone. The partially coated particles, which are then further lifted in the air stream and dried, settle out and descend to begin another cycle. The cycles are continued until the desired thickness of coating is achieved.

30 Although the present invention is not limited to any particular type, or brand, of fluidized bed coaters or coating processes, one type that has been found

to be particularly useful and is given by way of example only, is known as Wurster coaters or the Wurster process named after one of the original inventors, Dale E. Wurster. In this regard, see U.S. Patent 3,196,827 and some of the later patents relating to this coating technique such as U.S. Patents 5,236,503 and 5,437,889, all of which are incorporated herein by reference. In this process, the nozzle is located such that the travel distance of the liquid or suspension droplet from the nozzle is minimized. The coated particles are lifted on the air stream which dries the coating as the particles are carried upward. Because the system uses large volumes of air, it has a large drying capacity. Also, because the particles are separated from each other as they are carried on the air stream and coated, it is possible to coat a wide range of particle sizes including very small core particles (less than 50 microns) while at the same time controlling and minimizing agglomeration.

The preferred system comprises a conically shaped product container with an open ended cylindrical inner partition. An air distribution plate is located at the lower end of the production container to distribute the fluidization air between the inner and outer partitions. The majority of the air is channeled through the inner partition leaving sufficient air flow to suspend particles in the outer partition. Particles are drawn into the inner partition by the pressure differential created by the difference in air velocities between the two partitions. The particles are carried through the inner partition and into the expansion chamber. As gravity overcomes the force of the fluidizing air, the particles fall back into the outer partition where they are suspended in a slowly, downwardly moving bed. The coating composition of the present invention is added via a pneumatically atomized nozzle located at the center of the air distributor plate. The nozzle sprays upward, providing a co-current application of solution onto the particles. As atomized droplets of the coating composition contact the particles in the inner partition, they spread and coalesce on the particle surface. Excess moisture from the applied liquid is evaporated as the particles continue traveling through the system.

More specifically, a product container section opens upwardly into an expansion chamber and downwardly into a lower plenum chamber through a generally horizontally disposed air distribution plate having openings formed therethrough for the upward air flow from said lower plenum chamber into said product container section. The product container section includes a substantially cylindrical partition spaced above the air distribution plate for dividing the product container section into an inner up-bed area and an outer down-bed area. An upwardly discharging spray nozzle is mounted substantially centrally within the cylindrical partition. For more details on the process and the apparatus used in the process, see the previously mentioned U.S. patent 3,196,827 and U.S. Patents 5,236,503 and 5,437,889.

Another example is a rotor coater. The rotor coater (or spin disk coater) is used in a wide range of operations. Ideal for agglomeration, coating or granulating of any kind of powder. The rotor insert combines short processing times with consistent uniformity of product. As inlet air is introduced into the coater from the side wall to form an air curtain, a fluidizing motion is created along the wall of the rotor coater. This, on one hand provides the force to suspend the solid particles from falling through the slit and at the same time creates a mechanism to roll the particles over. The combination of centrifugal force generated by the spinning rotor, rotation speed, gravity and slit air create a rope-action, or whirling that helps the product to mix quickly and evenly into the cyclic movement of the rotor bed. The particle stream and its degree of fluidization are controlled by rotor speed, air volume and the air velocity at the rotor slit gap. Slit air controls the peripheral airflow during the process, assisting the spiraling motion of the bed while simultaneously drying the product. The slit air gap is adjustable by moving the air gap ring closer to or farther away from the rotor plate. As centrifugal force moves the product into the spray zone, the particles are coated by a peripherally mounted spray gun.

The range of core particle sizes for the catalyst of the present invention can range from 5 microns (0.005 mm) up to 20,000 microns (20 mm) with the preferred range being 0.03 mm up to 4.0 mm. Depending upon the size and density of the core particles, the operating conditions for the fluidized bed coating

process would be adjusted accordingly to maintain the desired fluidizing conditions coupled with the control of the drying conditions. It is also possible to carry out the coating process using a fluid bed coating technique which relies on mechanical means to produce the fluidization within the coating chamber.

5       The preferred material for producing the shell or film on the catalyst particles is an alumina colloidal dispersion or sol. However, other materials may be employed in the present invention such as clay minerals, zeolites, titania, zirconia, ceria, silica, magnesium oxide, rare earth oxides, carbon-based supports and their mixtures. The catalyst element in the coating composition may be used  
10 in the form of a sol or in the form of a liquid dispersion of small, non-colloidal particles preferably mixed with colloidal particles which serve as the binder. As an example, the suspended coating particles may be alumina particles from 2 millimicrons (2 nanometers) up to 10 or more micron size particles. The coating slurry may even contain milled particles of up to 100 microns diameter but  
15 preferably less than 10 microns. Typically, the coating material is a sol of a transitional alumina precursor, such as boehmite or pseudoboehmite formed with an average particle size of 2 - 100 nm (2 - 100 millimicrons). Another typical coating material is a slurry containing milled commercially available transitional alumina with an average particle size of about 4 microns, and containing 10-90%  
20 by weight colloidal alumina particles in the slurry on a water free basis. In the usual case of slurries in which the particles are larger than the sols, the slurry contains a separate binder phase which may actually be a quantity of alumina sol, or a binder created in situ by adding acetic or other acids to the transitional alumina slurry prior to milling of the alumina to reduce the particle size. As used  
25 herein, the term slurry includes sols as well as liquid dispersions of fine, non-colloidal size particles.

As indicated, an object of the invention is to produce a thin coating as well as a uniformly thick, homogeneous coating. The use of the fluidized bed coating process such as the Wurster process produces the uniform and homogeneous  
30 coating, and is capable of producing the desired thin coatings by merely controlling the duration of the coating cycle. The desired coating thickness may

vary depending upon the particular catalyst being produced, but the preferred range of thicknesses is between about 0.1 microns and 100 microns. In a preferred embodiment the film thickness is at least 10 microns.

5 In the fluidized coating process, the atomized spray of the slurry produces very fine droplets, perhaps on the order of 20-30 microns. In each pass of the support or substrate particles through the atomized spray of coating composition, only a small percentage of the surface of the core particle is coated, perhaps only 2 or 3%. The successive passes of the particles through the atomized spray and the drying of the coating between each pass produces the film. Determination of the  
10 BET (Brunauer, Emmett and Teller) surface area of samples removed at different times demonstrates that there is a uniform rate of deposition of the slurry onto the core particles and that there is a continual build-up of the layers of the shell. It is further shown by cross-sectional scanning electron microscopy that when using the fluidized bed coating technique the deposition of the gamma-alumina sol onto  
15 alpha-alumina spheres according to the present invention produces a film or shell which is exclusively on the exterior surface of the alpha-alumina spheres and does not penetrate into the pores.

In the embodiment of the invention where the film is formed from an alumina sol containing boehmite or pseudoboehmite, this precursor is treated in  
20 air, or in an inert gas atmosphere, or in a mixture of the two gases, in each case with or without steam, to convert the boehmite or pseudoboehmite phase in the thin film to a transitional alumina phase. Temperatures of 200-1100°C can be employed to give the desired combination of physical and chemical characteristics in the transitional alumina film. The gas atmosphere may contain  
25 the steam at different amounts to control the conversion process to the most desirable surface area and pore size within the film according to known techniques.

In the case where the thin films of the instant invention, formed on a relatively inert core, are transitional aluminas, then the film can be converted to a  
30 solid acid catalyst by a wide number of techniques that are well known to those skilled in the art. In this regard, see U.S. Patents 2,999,074 (Block), 4,433,191

(Eleasar), 4,347,399 (Rice) and 4,179,581 (Mitzchel). In general, the film can be converted to an acid catalyst by halogenating or sulfating.

As an example, the transitional alumina films which have been formed can be reacted in the gas phase with such reactive chlorine containing species as carbon tetrachloride, chloroform, sulfonylchloride, hydrogen/hydrogen chloride mixtures, chlorine gas with/without added oxygen, etc. The time of treatment, the flow rate of the gas, and the temperature of treatment for a given film thickness are all variables which are known to effect the amount of retention of chlorine within the film and directly impact on the acidity of the film. Similarly, treatment can be carried out with fluorine containing gases such as carbon tetrafluoride, boron trifluoride, hydrogen fluoride, etc. Solids that can be vaporized/sublimed onto the alumina film can also be used to prepare solid acids by deposition of the solid within the thin film. Examples would be aluminum trichloride, antimony pentafluoride, and hydrogen boron tetrafluoride. In the application of these thin films as solid acids, it is known that there may be a continuous addition of the chloride or fluoride-containing compounds during the reaction to maintain the activity of the solid acid catalyst in such applications as paraffin and olefin isomerization, aromatics alkylation, and gasoline alkylation.

In addition, the chlorination or fluorination can be carried out by treatment in a solvent containing reactive chlorination species such as alkyl aluminum chloride, sulfonyl chloride, etc. For these solid acid catalysts prepared by treatment in the gas phase and/or by treatment in a solvent, post treatment at different temperatures between 100 - 900°C may be beneficial in a variety of gas atmospheres including hydrogen, hydrogen chloride, or their mixture, air or mixtures of air diluted with an inert gas such as nitrogen, or treatment in an inert gas such a nitrogen or helium. the duration of treatment of the catalyst, the temperature of treatment, and the flow rate of the treatment gas may be used to control the acidity of these catalysts for different applications.

In the case of a thin film of zirconia or titania, preferably anatase, made on a relatively inert core, it is possible to convert the film to a strongly acidic solid acid catalyst by treatment of the catalyst with ammonium sulfate, sulfuric acid,

etc. and then to treat at temperatures between 400 and 800°C to form a strongly acidic solid acid catalyst. The following references exemplify the range of solid acids made by sulfation of zirconia; (1) Escalona Platero, E., Penarroya Mentrut, M., Otero Arean, C., and Zecchina, A., J. Catal. 162, 268-276 (1996); (2) Hsu, C.Y., Heimbruch, C.R., Armes, C.T., and Gates, B.C., J. Chem. Soc. Chem. Comm. 1645, (1994); (3) Bensitel, M., Saur, O., Lavealley, J.C., and Mebilon, G., Mater. Chem. Phys. 17, 249 (1987); (4) Escalona Platero, E., and Penarroya Mentrut, M., Catal. Lett. 30, 31 (1995); (5) Escalona Platero, E., and Penarroya Mentrut, M., Mater. Lett. 14, 318 (1992); and (6) Otero Arean, C., and Escalona Platero, E., Adsorption-Sci. Technol. 1, 159 (1984).

Another example of the present invention involves the conversion of the alumina thin films to nickel catalysts which are particularly useful for hydrogenation. Many hydrogenation reactions are very fast reactions which benefit from having small catalyst particles. The process of the present invention for forming thin film catalyst particles is one approach to having effectively small catalyst particles. The benefits are a lower catalyst inventory for a given reactor volume and lower rates of catalyst deactivation due to fouling of the catalyst surface.

Nickel catalysts on an alumina support formed by prior art processes are currently used commercially such as in catalytic distillation. The dispersion of the nickel is a key to the effective utilization of the nickel content since the dispersion directly relates to the amount of nickel surface area available for catalysis. Also, the dispersion is directly related to the size of the nickel metal particles whose exterior surface is available for catalytic function in hydrogenation. For a nickel catalyst with a dispersion of 30%, the nickel particles are about 2 nm in diameter. Information on the nickel metal dispersion allows a comparison of the effectiveness of the nickel catalysts prepared according to the present invention and the effectiveness of commercial nickel catalysts that do not possess the thin film of the present invention. In addition, it is known that nickel metal dispersions are approximately 30% for nickel/alumina catalysts similar in surface area to those produced by the present invention for nickel loadings of 14 to 18 wt. percent



based on the weight of the thin film. In this regard, see U.S. Patent 4,073,750 which also discloses the use of nickel metal precursors and the conversion to the nickel metal which can also be used in the present invention.

Although in a preferred embodiment, the substrate or support is coated  
5 with a thin film or coating of a catalyst element by the use of a fluidized bed coating technique, the present invention insofar as it is directed to the use of a coating composition which includes a polymer is not limited to such a fluidized bed coating technique even though such coating composition provides particular advantages when used with a fluidized coating technique. Thus, for example, the  
10 coating composition of the present invention may be employed for coating a catalyst element on a support by coating techniques such as dip coating or conventional impregnation.

The coating composition of the invention is particularly advantageous wherein the method of coating applies a shear force to the coating during  
15 application of the catalyst or catalyst precursor to the substrate.

In a preferred embodiment, a thin film of a catalyst element is coated onto a porous substrate without essential penetration of the catalyst element into the pores of the porous support. In such a preferred embodiment, the catalyst element dispersed in a liquid (water or polar organic solvent) is applied to the porous  
20 substrate as a spray or droplets under conditions such that the liquid is rapidly evaporated after application to the substrate. For example, application of the coating composition to the substrate with rapid evaporation of the liquid may be effected in a fluidized bed coating apparatus or in a rotor coater, as hereinabove described. In such a procedure the coating composition may or may not include a film forming  
25 polymer and preferably includes a film forming polymer.

The invention will be further described with respect to the following examples; forever the scope of the invention is not to be limited thereby:

### Example 1

#### 1. Alumina Sol

The aluminum sol [Condea 23N4-20 sol] used has a solid content of 20 weight percent as alumina. To obtain diluted sol, the 20 weight percent sol was added to the required amount of distilled water drop-wise while under constant stirring. When a film forming polymer is employed the polymer is a polyvinyl pyrrolidone (Povidone K-90 from BASF) dissolved in distilled water to make a 1% solution. 1% Povidone solution and 20% Condea sol were mixed in equal amount to give 10% sol and 0.5% Povidone.

#### 2. Alumina Plates

High purity alpha alumina plates in 2" x 2" (Coors Corporation, Colorado) were used for coating experiments. They were used without further treatments.

#### 3. Coating

Dip coating was used to soak the alumina plates in sols. After removal from the coating, excess sol was removed by shaking and the plates were dried under ambient conditions. However, in order to simulate fluid bed coating conditions, an air knifing technique was used to apply high pressure air (~80psi) to newly formed fluid film on alumina plate surface to blow away excess sol and dry the coating.

## RESULTS

#### A. Dip Coating

Figure 1 summarizes the results for dip coating of alumina plates with a number of different sols.

#### B. Effect of Polymer

Addition of 0.5% Povidone (PVP) has led to higher coating efficiency (from 2.5 $\mu$ m to 3.5 $\mu$ m).

**C. Air Knifing**

Figures 2 and 3 summarize the results for multiple coating with air knifing at approximately 60-80 psi of alumina plates with a number of different sols.

**D. Effect of Polymer Addition**

5 Sol with 500 ppm sodium added including PVP gave a much higher coating efficiency than the one free of PVP (coating thickness 12  $\mu\text{m}$  v. 2.4  $\mu\text{m}$ )

**E.** The addition of sodium reduces coating efficiency.

**Example 2****1. Sols**

10 Unless otherwise stated, the coating sol contained 10% Condea 23N4-20 and 150ppm of sodium nitrate and 0.05-1% of polymer additives.

**2. Alumina Plates**

High purity alpha alumina plates in 2" x 2" ( Coors Corporation, Colorado) were used for coating experiments. They were used without further treatments.

15 **3. Coating**

Each coating was defined as dip coating followed by air knifing at 75-80 psi to dryness before applying the next coating. A total number of nine coatings were applied, then dried at 150°C before calcining at 550°C for a minimum of 3 hours. The coating thickness was estimated based on weight gain and a density of  
20 1.5 g/cm<sup>3</sup>.

**RESULTS****A. Hydropypropyl methyl cellulose (OPADRY)**

Figure 4 shows the effect of OPADRY addition on coating efficiency.

### Example 3

#### Wurster Coater:

Table 1 and Table 2 summarize the results in Wurster coating. In each run, an amount of 6 kg of alpha alumina microspheres (1 mm) from Norton was charged to the Glatt 7" HS Wurster coater. The alumina sol used for coating was from Condea Vista, containing 20%  $Al_2O_3$ .

In a typical run, the inlet air temperature was controlled to 60-70°C and flowing at 200-220 ft<sup>3</sup>/min, and the relative humidity of the inlet air was adjusted such that with a spray rate of 60-70 g/min. the product temperature was 34-36°C and relative humidity was 40%. The spray of alumina sol started once the bed temperature was equilibrated. A coating loading of 20% in the finished product was targeted. During the coating, periodically, samples were taken for microscopic observation moisture content determination, and quality control.

The mixture containing alumina sol and polymer additives was made by combining required amounts of 20% alumina sol and predispersed polymer sol or solution.

In the table, the amount of coating expected is based on the amount of alumina sol applied, while that measured is determined by surface area measurement.

The coating characteristics are assessed using a stability determination protocol and microscopic observation. The stability determination protocol consists of shaking an amount of 2-5 g of coated product after being calcined at certain temperatures in a 50 cc Pyrex container vigorously for an approximately 100 times.

If the coated product survives this test it would have survived the cold flow test designed to mimic liquid phase moving bed applications.

Microscopic observation can show whether cracking occurred, chipping or spalling occurred, fines formed.

#### Rotor Coater

Table 3 summarizes the results in rotor coating. The coating was carried out using a Vector 12" FLO rotor coater. In each run, an amount of 3 kg of alpha alumina microspheres (1 mm) from either Norton or Condea-Vista was charged. In a typical run, the inlet air temperature was controlled to 60-70°C and flowing at 120-220 ft<sup>3</sup>/min. The operating conditions were adjusted such that the product bed temperature was around 40-50°C and relative humidity below 40% and the rotor speed was varied from 150-350 rpm. Spray of alumina sol started once the bed temperature was equilibrated. A coating loading of 20% in the finished product was targeted. During the coating, periodically, samples were taken for microscopic observation and moisture content determination.

Table 1

Summary of Coating Results Using Wurster Coater with and  
Without PVP Additive

0.5% PVP	Coating (wt%) Expected	Coating (wt%) Measured by BET	Coating Characteristics
Yes	20	20.8	Stable coating, no fines
No PVP	20	<15	Unstable coating, fines formation

**Table 2**  
**Summary of Coating Results Using Wurster Coater**  
**With and Without Opadry Additive**

0.9% Opadry	Coating (wt%) Expected	Coating (wt%) Measured by BET	Coating Characteristics
Yes	20	22.1	Stable coating, little fines formation
No Opadry	20	<15	Unstable coating, fines formation

**Table 3**  
**Summary of Coating Results Using Rotating Disk Coater**  
**With and Without PVP Additive**

0.9% PVP	Coating (wt%) Expected	Coating (wt%) Measured by BET	Coating Characteristics
Yes	20	19.8	Very stable coating, no fines
No PVP	20	13.9	Unstable coating, fines formation, agglomeration

The present invention is particularly advantageous in that it is possible to produce a thin film coating on a substrate under conditions in which a shear force is generated during the coating process with reduced cracking of the film and improved adherence of the film to the substrate.

Although Applicant does not intend that this invention be limited by any reasoning it is believed that the polymer forms a web or complex of filaments in the composite that functions to reduce or eliminate cracking forces on the coating. It is believed that the polymer provides flexibility during the drying process and/or in subsequent operations that reduces or eliminates cracking that would occur without the presence of the polymer.

After the coating process, the polymer that is now present may be eliminated by heating of the particles to remove the polymer, e.g., heating at a temperature of above 100°C up to 1300°C, preferably in air or air diluted with an inert gas such as nitrogen, or in an inert gas, or in these gases with variable levels of steam present.

5

Numerous modifications and variations of the above described invention are possible within the scope of the appended claims and, therefore, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

**What Is Claimed Is:**

1. A process for coating a substrate with a thin film of a catalyst element, comprising:

coating a thin film of a catalyst element onto a substrate by coating  
5 with a coating composition comprising catalyst element particles, at least one film forming polymer and at least one member selected from the group consisting of water and a polar non-aqueous solvent wherein said catalyst element is at least one member selected from the group consisting of an unsupported catalyst, an unsupported catalyst precursor, a catalyst support, a supported catalyst precursor  
10 and a supported catalyst, said film forming polymer being present in an amount effective to prevent spalling of the catalyst element film on the substrate wherein when said member is an unsupported catalyst, said unsupported catalyst is other than a metal sol.

2. The process of Claim 1 wherein said member is water.

15 3. The process of Claim 2 wherein said coating is effected by applying the coating composition to a fluidized bed of said substrate.

4. The process of Claim 2 wherein at least a portion of the catalyst element is in the form of a sol.

20 5. The process of Claim 2 wherein the at least one film forming polymer is polyvinyl pyrrolidone.

6. The process of Claim 5 wherein the coating is applied to provide a coating thickness of less than 250 microns.



7. The process of Claim 6 wherein the substrate is a porous substrate and the coating is applied without essential penetration of the coating into pores of the substrate.

8. The process of Claim 7 wherein the catalyst element is an inorganic catalyst element.

9. The process of Claim 2 wherein the film forming polymer is water soluble.

10. The process of claim 2 wherein the film forming polymer is hydropypropyl methylcellulose.

11. The process of Claim 2 wherein the film forming polymer is water dispersible.

12. The process of Claim 2 wherein the film forming polymer is present in an amount of from 0.2 to 5 percent, by weight.

13. The process of Claim 2 wherein the coating is effected in a rotating disk coater.

14. A coating composition comprising:

a catalyst element in particulate form a film forming polymer, and at least one member selected from the group consisting of water and a polar non-aqueous solvent, said film forming polymer being present in an amount effective to prevent spalling of the catalyst element when applied as a thin film to the substrate, said catalyst element being selected from the group consisting of an unsupported catalyst, an unsupported catalyst precursor, a catalyst support, a supported catalyst precursor and a supported catalyst, wherein when said member is an unsupported catalyst, said unsupported catalyst is other than a metal solv.

15. The composition of Claim 14 wherein the member is water.

16. The composition of claim 15 wherein the at least one polymer is present in an amount from 0.2 to 5 percent, by weight.

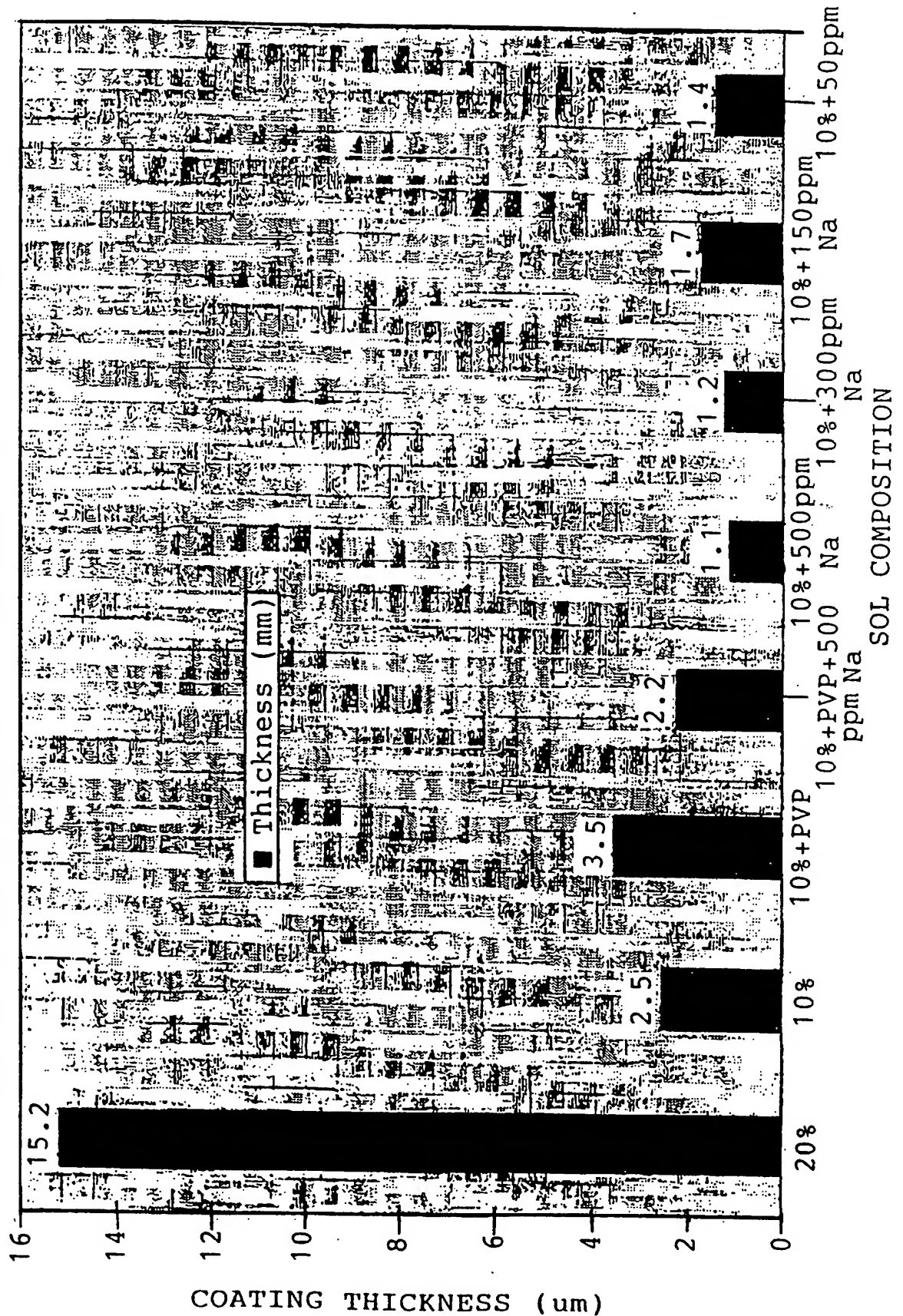
17. A process for producing a thin film of a catalyst element on a substrate  
5 comprising:

applying a coating composition comprising a catalyst element dispersed in a liquid to a porous substrate as liquid droplets under conditions effective to rapidly evaporate said liquid after application to the substrate to produce a thin film of said catalyst element on said substrate without essential penetration  
10 thereof into pores of the porous support, said catalyst element being at least one member selected from the group consisting of an unsupported catalyst, an unsupported catalyst precursor, a catalyst support, a supported catalyst precursor and a supported catalyst, wherein when said member is an unsupported catalyst, said unsupported catalyst is other than a metal sol.

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FIG. 1

COATING CHARACTERISTICS OF DIFFERENT SOL (DIP COATING)



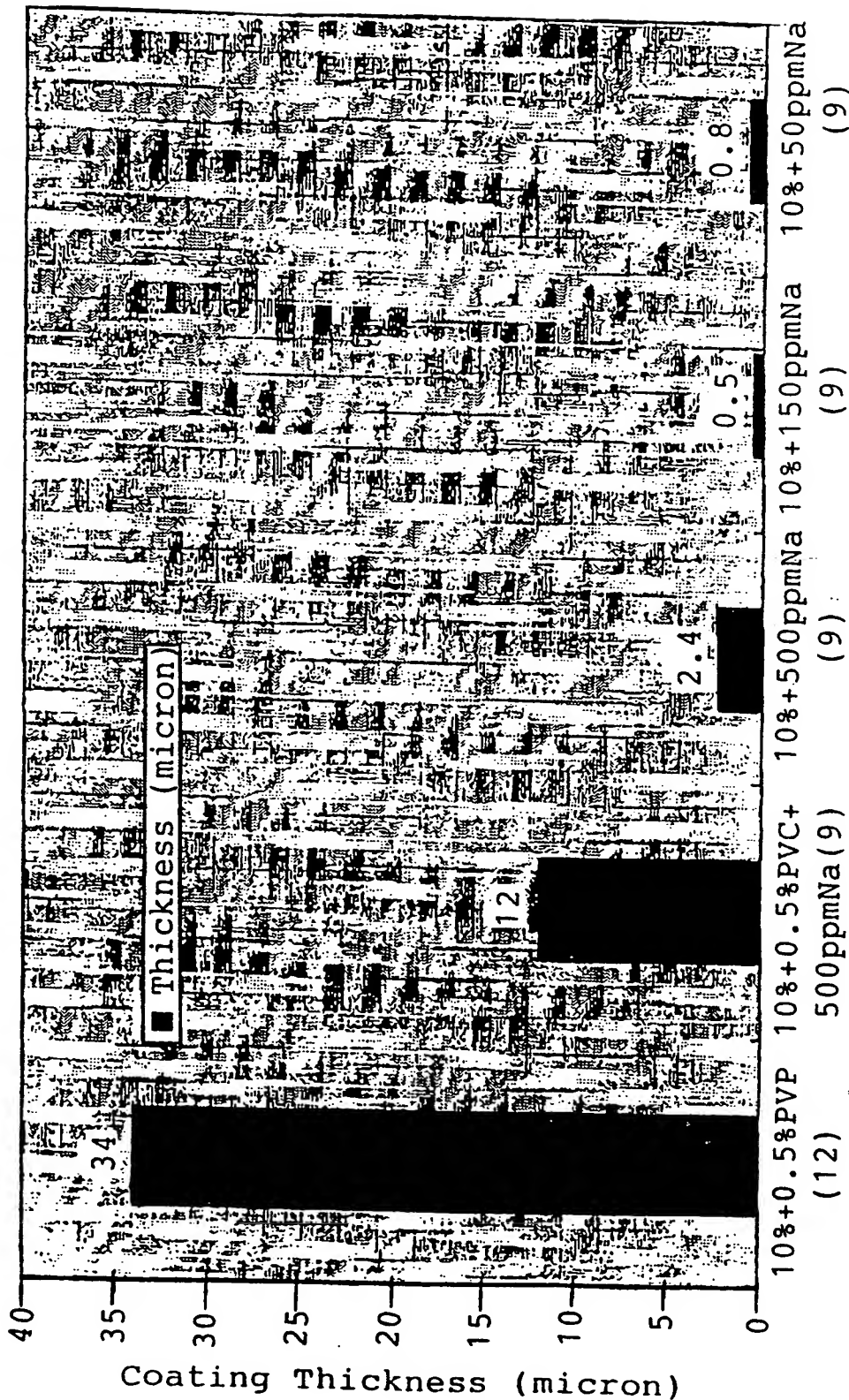
COATING THICKNESS (um)

SUBSTITUTE SHEET (RULE 26)

2 / 4

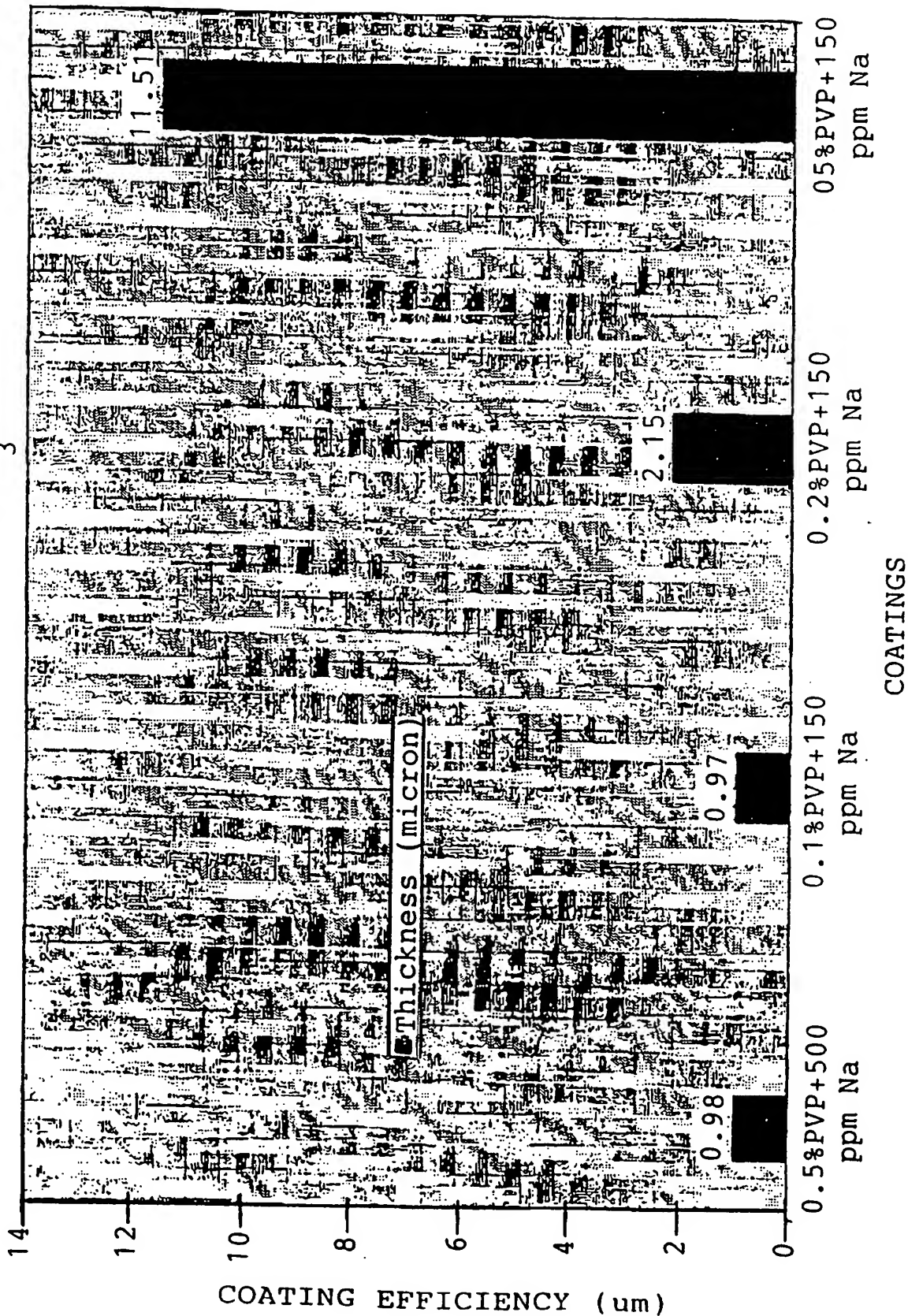
FIG. 2

COATING CHARACTERISTICS OF DIFFERENT SOLS (AIR KNIFFED)



SOL COMPOSITION

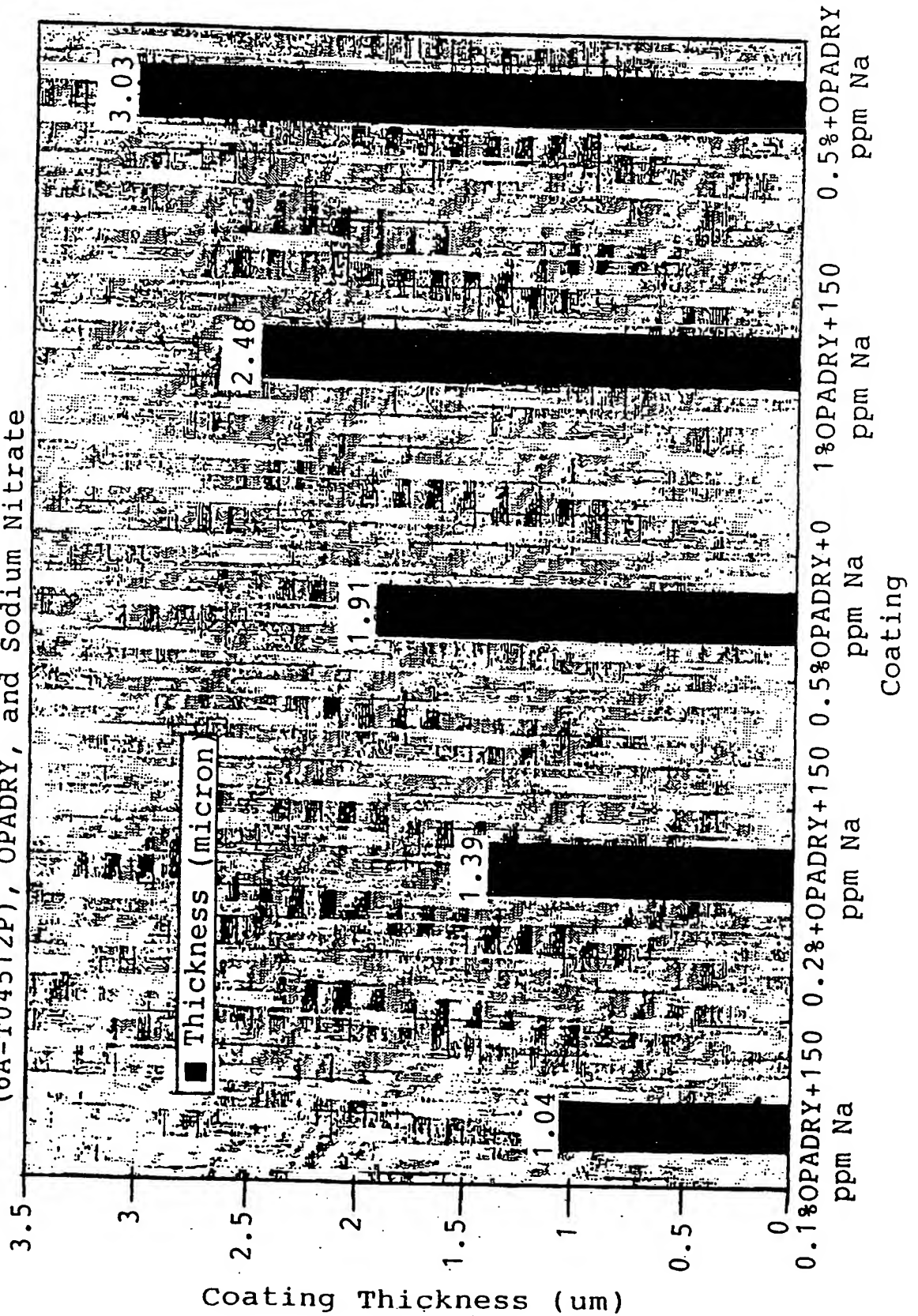
FIG. 3 COATING CHARACTERISTICS OF 10% CONDEA SOL (6A-T04512P)  
+PVP+NaNO<sub>3</sub>



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FIG. 4

Coating Characteristics of Mixture containing 10% Condea  
(6A-T04512P), OPADRY, and Sodium Nitrate



PCT/US 99/26508

IPC 7 B01J37/02

**According to International Patent Classification (IPC) or to both national classification and IPC**

**B. FIELDS SEARCHED**

**Minimum documentation searched (classification system followed by classification symbols)**

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 134 413 A (ATOMIC ENERGY AUTHORITY UK) 15 August 1984 (1984-08-15)	1,2,4,8, 11,12, 14-16
Y	the whole document	1-4,6-8, 11,12, 15-17
	---	
X	WO 98 14274 A (ABB LUMMUS GLOBAL INC) 9 April 1998 (1998-04-09)	17
Y	the whole document	1-4,6-8, 11,12, 15-17
	---	
X	WO 95 13874 A (BASF AG ; KORMANN CLAUDIUS (DE); WETTLING THOMAS (DE); SCHWAB EKKEH) 26 May 1995 (1995-05-26) page 3, line 8 -page 5, line 10; examples 1-3	1,2,5,8, 9,11,12, 14-16
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

<sup>o</sup> Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z document member of the same patent family

Date of the actual completion of the international search

17 March 2000

Date of mailing of the international search report

0 4. 04. 90

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/26508

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 521 618 A (ARNTZ DIETRICH ET AL) 4 June 1985 (1985-06-04) column 2, line 55 -column 3, line 59 column 4, line 38 - line 52 column 4, line 67 -column 5, line 26 ---	1-3,8, 13-15,17
P,X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 03, 31 March 1999 (1999-03-31) & JP 10 337478 A (SUMITOMO METAL IND LTD), 22 December 1998 (1998-12-22) abstract -----	1,2,4,5, 8,9,14



# INTERNATIONAL SEARCH REPORT

Int. l. application No.  
PCT/US 99/26508

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

**1. Claims: 1-16**

Independent claim 1 and dependent claims 2-13 relate to a process for coating a substrate with a thin film of catalyst comprising a film forming polymer.

Independent claim 14 and dependent claims 15-16 relate to a coating composition comprising a catalyst element in particulat form and a film forming polymer.

**2. Claim : 17**

Independent claim 17 relates to a process of producing a thin film of catalyst on a substrate comprising the application of the catalyst element as liquid droplets under conditions effective to rapidly evaporate said liquid after application.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/26508

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JP 10337478 A	22-12-1998	NONE	

THIC 777 (ISPTO)